

HYDROGASIFICATION OF OIL SHALE

S. A. Weil, H. L. Feldkirchner, and P. B. Tarman

Institute of Gas Technology
Chicago, Illinois 60616INTRODUCTION

In the early 1960's, the Institute of Gas Technology (IGT) carried out an extensive research program for the American Gas Association (A.G.A.) on the direct hydrogasification of, primarily, Colorado oil shale (3). IGT used laboratory and bench-scale equipment. In the bench-scale tests, using cocurrent hydrogen/shale contacting, we were able to gasify about 65% of the organic carbon in the oil shale. About 15% was converted to light aromatic liquids, and about 20% remained in the spent shale. The major variable controlling the conversion of organic matter to gas was the hydrogen/shale ratio.

Economic studies indicated that the cost of pipeline gas from oil shale was promising. However, there were two major disadvantages in cocurrent operation:

- Approximately 20% of the available energy in the raw shale was not recovered, and it was questionable whether the residual organic matter could be economically recovered as process fuel.
- Most of the heat used in preheating the shale to reaction temperature would be lost as sensible heat in the hot spent shale, which would discharge at 1100°-1300°F.

This study was initiated, therefore, to investigate the technical and economic feasibility of producing synthetic pipeline gas from oil shale by hydrogasification, using countercurrent gas-solids contacting and excess hydrogen. It was expected that the use of excess hydrogen with controlled, countercurrent shale heating and cooling would result in increased organic carbon removal from the shale and improved heat recovery - resulting in improved overall process efficiency compared with previous processes. The use of excess hydrogen would require hydrogen recycle, but would probably permit operation at lower pressures and thus reduce plant capital equipment costs (relative to processes using cocurrent gas-solids contacting and near-stoichiometric hydrogen/shale ratios). Preliminary economic studies based on a 20-25 gal/ton Fischer Assay oil shale indicate that raw material costs would be much greater than reactor costs. Thus, it would be desirable to convert as much of the organic matter content of the shale as possible. This would also be desirable in view of long-range energy conservation principles.

Initially, we carried out material and energy balance, heat transfer, and other process design calculations to determine the general areas for the most efficient operation. Next, we conducted a series of tests using a thermobalance to determine the effects of temperature, pressure, hydrogen partial pressure, and the rate of shale heat-up on the rate and ultimate level of kerogen conversion. Ways to minimize undesirable mineral carbonate decomposition reactions were also studied. Finally, a series of tests was conducted in a 4-inch-diameter reactor to determine the effects of process variables on the yields of gaseous, liquid, and solid products and their rates of production from oil shale kerogen. In this paper, we present test results relating process variables to product yields and product properties.

THERMOBALANCE STUDIES

Experimental

The test program to study the effects of temperature, hydrogen pressure, particle size, and heat-up rate on the rate and extent of kerogen removal from the shale was carried out with a thermobalance, as diagrammed in Figure 1. The design and operation of the equipment have been described earlier (2).

In most of the runs, the shale sample (as pebbles) was contained in a stainless-steel wire-screen basket $1/4$ to $3/8$ inch in diameter and 3 inches in height. The reactor section was brought to the desired initial temperature with a stabilized gas flow stream at about 10 SCF/hr. The sample was lowered into the reactor and the power into the heating elements adjusted to achieve the desired heat-up rate. The heat-up rates used included slow (about $15^{\circ}\text{F}/\text{min}$), fast (about $35^{\circ}\text{F}/\text{min}$), and very rapid, in which case the sample was lowered quickly into a preheated reactor. In the last case, it is estimated that about 40 s were required for the sample to attain reactor temperature. After a prescribed time or upon reaching a prescribed temperature, the sample was raised into a cool region above the reactor, effectively stopping further reaction.

The sample was weighed before and after each run, and the residue was analyzed for carbon, carbonate, hydrogen, and ash. During the run, the sample weight and temperatures (using four thermocouples which surrounded the sample) were continuously recorded.

After selection, the shale rocks were crushed, sieved, and divided by riffing into small samples. The shale samples were 2.5 to 3 g in weight and $-6+10$ in U.S. Standard sieve size. Random samples chosen for chemical analysis gave the following average composition. (See Table 1.)

Table 1. SHALE COMPOSITIONS

Composition	Rich Shale, 52 gal/ton	wt %	Lean Shale, 11 gal/ton
Organic Carbon	21.06		5.40
Hydrogen	2.84		0.99
Carbon Dioxide	12.54		18.17
Sulfur	0.83		0.45
Calcium	6.3		8.8
Magnesium	3.3		4.8
Ash	60.0		74.0

It is estimated that the rich shale has 40.3% potentially volatile material of which 12.5% is CO_2 and 27.8% is other volatile components (OVC). Of the CO_2 , 53% is from the CaCO_3 and 47% is from the MgCO_3 .

Results of Rich-Shale Studies (Total Conversion)

The weight loss vs. time curves and the shale residue compositions were determined for a wide variety and range of conditions. The major variables were hydrogen pressure, gas composition, heat-up rate, initial temperature, and maximum temperature.

A typical time-temperature-weight loss relation is shown in Figure 2. Characteristics common to all heat-up rate runs are the onset of significant weight loss at 700°F and a rapid rate of weight loss between 800° and 1000°F, followed by a much slower rate until about 1100°F when the rate increases again significantly. The thermobalance measures only weight changes, so the curve represents weight loss due to CO_2 as well as to kerogen removal. In any given run, only the final amounts of each component are known. Other runs were made at the same operating conditions and temperature histories except that the samples were withdrawn from the reactor at different temperatures. From their residue analyses, additional points were added to Figure 2 to show an estimate of the weight loss due to volatile components other than CO_2 (OVC) and of that due to CO_2 . These results show that there is a sharp drop in the rate of kerogen removal above about 1000°F. Furthermore, although there is still organic carbon left, there is not much more weight loss beyond 1200°F. The above behavior appears to apply to all of the runs made.

Under almost any conditions, the organic carbon recovery in a hydrogen atmosphere was at least 87%. The maximum recovery in a helium atmosphere was 77%.

From the variations of time-temperature paths, the following qualitative characteristics were found to be true in a hydrogen atmosphere.

- a. Direct exposure (hence, very rapid heat-up) to temperatures of 1300°F or higher leaves about 13% of the original carbon in the residue regardless of exposure time.

- b. Soaking of the shale sample for 1 hour or more at 700° or 800°F (or very slow heat-up) improves kerogen conversion at higher temperatures.
- c. Soaking at low temperatures without heating above 1000°F results in as much kerogen recovery as direct exposure to high temperatures (13% of original carbon remaining).
- d. Higher hydrogen pressures resulted in lower residual organic carbon.

Figure 3 shows the residual organic carbon for the range of hydrogen pressures and heat-up rates studied. In all of these runs, the final temperature was 1300°F. It is apparent that the high-temperature kerogen recovery is extremely pressure sensitive.

The carbonate decomposition does not become significant until 1000°F and, as would be expected, is greater for longer periods at temperatures above 1000°F. There appears to be a qualitative correspondence between residual organic carbon and residual CO₂. For example, it is noticeable in comparing the helium runs with the pure hydrogen runs which have the same time-temperature path to 1300°F. The former resulted in 23% residual carbon and 80% residual CO₂. The latter resulted in 7% residual carbon and 34% residual CO₂. In two areas, this rough correspondence does not hold; at low hydrogen pressure or very rapid heat-up rates, the conditions are relatively poor for kerogen recovery and very good for carbonate decomposition. Also, kerogen recovery is enhanced relative to CO₂ generation when the shale is soaked in hydrogen at temperatures below 1000°F and above 700°F. Figure 4 shows that low carbonate decomposition (less than 20% of original) can be achieved in simple heat-up paths, but at the expense of leaving 8% of the shale's organic carbon. To obtain lesser amounts of carbons, the most favorable path for minimal CO₂ generation is that of long soaking at 800°F before heating to higher temperatures. In that case, a residual carbon of only 3% of the original carbon can be achieved with 65% carbonate decomposition, as compared to almost 100% carbonate decomposition to achieve the same residual carbon by uniform heat-up.

An alternative method of suppressing carbonate decomposition is possible because the decomposition pressure of CaCO₃ is low enough to be overcome by a trace of CO₂ in the gas phase. When 2% CO₂ was added to the feed gas (10-psia CO₂), the carbonate decomposition was much less than in the corresponding pure hydrogen runs.

It should be noted, however, that while the carbonate decomposition was repressed, the kerogen recovery was also reduced relative to the pure hydrogen runs. Thus, the net improvement was not as striking as implied by the CO₂ repression (Figure 4).

Results of Rich-Shale Studies (Kinetics)

Low-Temperature Kerogen Recovery

In the heat-up runs, there appears to be a significant decrease in weight-loss rate when the sample reaches about 1000°F and has lost about 25% of its original weight (Figure 2). In constant-temperature runs below 1000°F, there appears to be a limiting weight loss, again about 25% of the rich shale. In this discussion, this portion of the recovered kerogen (and any other materials that comprise this weight loss) is referred to as the low-temperature weight loss or kerogen recovery.

In Figure 5, the low-temperature weight-loss rates for several heat-up runs are shown as functions of the extent of weight loss. The range of operating conditions includes 15° to 35°F/min temperature-rise rates and 20 to 500 psig pressures. In all cases, the low-temperature rate can be extrapolated to zero in the region of 23 to 25% weight loss. The actual rate goes through a minimum in this region (which also corresponds to 1000° - 1100°F), the subsequent rise being due to the CO₂ generation that begins at these temperatures and increases very rapidly. (See Figure 2.)

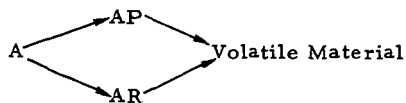
In Figure 6, similar data are presented at higher conversions for the constant-temperature runs at 800°, 900°, and 1000°F. Again, the rate of weight loss appears to become zero at about 25% weight loss. However, at 700°F the extrapolated weight loss at a zero loss rate was significantly lower than in the other runs, being about 11% rather than 25%.

It is apparent that, at temperatures of at least 800°F and, at most, 1000°F, a definite fraction of the kerogen is capable of being removed and will be removed if enough time in a hydrogen atmosphere is allowed. Furthermore, if any more kerogen were to be recovered at temperatures below 1000°F, it would require an additional time that is an order of magnitude greater than that needed for the low-temperature kerogen recovery.

In the case of the rich shale, the low-temperature weight loss, on the average, is 25.0% and (as are all kinetic data) is based on thermobalance data rather than on chemical analysis. There was no way to identify the components in this 25% from the data taken.

The randomness of the extrapolated values about 25%, regardless of temperature, makes it safe to assume that no portion of that 25% is CO₂. Of the other volatile components, 25% of the 28% in the original feed may constitute the low-temperature kerogen, leaving 3%. This value is supported by the results of runs in which the shale was at temperatures high enough to achieve full low-temperature weight loss (900°-1000°F), but inadequate to go any further. In these, the final OVC was 3.3 to 3.4%.

Attempts to devise a kinetic scheme for the low-temperature kerogen recovery in hydrogen have been made, but have not been successful. The constant-temperature data appear capable of description by a linear combination of first-order exponential terms as might result from a mechanism such as -



where AP and AR represent two different intermediate species. However, the determination of the appropriate kinetic parameters from the data proved to be very sensitive, and a satisfactory fit of the data has not been achieved.

High-Temperature Kerogen Recovery

The thermobalance data permit examination of the kinetics at low temperatures (1000°F) because of the fortuitous fact that no CO₂ is generated in that region. Above 1000°F, the CO₂ generation precludes any kerogen-generation rate data. Any analysis of the high-temperature kerogen recovery must be based solely on the residue analyses.

Among the runs with rich shale in hydrogen, a surprisingly large number resulted in residual organic carbons of about 2.7% of the original sample. These included -

- a. Instantaneous heat-up runs that did not have a reasonable time below 1000°F
- b. Runs at low hydrogen pressures
- c. Constant temperature runs below 1000°F

Runs in which temperatures higher than 1000°F were reached in hydrogen atmospheres left this amount or less residual carbon. It is very reasonable to identify the 2.7% residual carbon of the rich shale with the residual of the low-temperature kerogen recovery. Possibly fortuitously, the low-temperature OVC residual of 3% is approximately the same fraction of the original OVC as the 2.7% residual carbon is of the original carbon.

Eighteen runs at 500 psig with the rich shales resulted in residual carbon contents significantly lower than 2.7%. Simple relationships between the residual carbon and temperature history were sought, but not found. One characteristic of the results is that comparable conversions can be obtained in shorter time periods if the sample is uniformly heated from 600° to 1300°F than if it is dropped into 800°F or higher, held there, and then heated to 1300°F. This, together with the fact that we could not obtain high conversion (of the potential 2.7% high-temperature product) with long times at high temperatures, implies competing reactions are involved - one to the product or its precursor and the other to residual carbon. To even qualitatively explain both heat-up and constant-temperature run results, it is necessary to assume that the basic competing reactions are fast and that the ultimate conversion is determined within a few minutes of exposing the shale to reaction temperatures (probably above 600°F).

Results of Lean-Shale Studies

Because of the small fraction of organic carbon in the original sample and the correspondingly small amount of carbon in the residue, it is difficult to be sure of the significance of differences in the residual carbon among the runs. Certainly, qualitatively, there are many similarities with the results with the rich shale. Among these are -

- a. A residual carbon which is about twice as great in an inert gas (helium) as in hydrogen is obtained.
- b. Without low-temperature exposure, 89% of the organic carbon can be recovered compared with 87% for the rich shale.
- c. Seven percent of the carbon remains in fast heat-up runs and 3% in slow heat-up runs. The rich shale showed 7.3% and 3.6%, respectively.
- d. CO₂ generation is suppressed by CO₂ in the feed gas, but with a penalty in kerogen recovery.

There is other behavior which is different. Most noticeable is a much lower CO₂ generation rate in the lean shale. Only very long exposures at high temperatures resulted in CaCO₃ decomposition. In most of the runs only 65% of the MgCO₃ decomposed, while in the rich shale all the MgCO₃ always appears to decompose if the sample reaches 1300°F.

In the fast heat-up runs of the lean shale, there appears to be a smaller fraction of kerogen recovery above 1000°F than one would expect from the rich-shale work, implying a difference in the low-temperature kerogen kinetics.

BENCH-SCALE TESTS

A flow diagram of the bench-scale unit is shown in Figure 7. The unit consists primarily of a hydrogasification reactor with associated equipment for feeding oil shale and hydrogen and measuring their flow rates and for collecting and measuring the quantities of residual shale, liquid products, and product gas. Simple controls were used a) to maintain reactor temperatures at the desired values, b) to maintain feed rates at constant values, c) to maintain constant reactor pressures, and d) to collect representative samples of the feed and product gases.

The reactor (Figure 8) consists of a cold-pressure shell, with a 24-inch-ID and about 23 feet long, containing an Incoloy 800 internal reactor tube (4-inch ips, Schedule 40) which is heated by a seven-zone electric heater. The details of the design and operation of this reactor have been described previously (1). Each individually controlled zone is 31 inches long and has an ID of about 7 inches. The reactor pressure and the bed-pressure drop are recorded continuously as are the reactor temperatures. A total of 32 thermocouples is attached to the outer tube wall. Several internal thermocouples were installed during the test program. These temperatures were recorded continuously along with temperatures on other major pieces of equipment.

Shale was fed by a screw feeder from a pressurized hopper, which was filled before testing with sufficient shale for the entire run. The cold shale entered the top of the reactor and was preheated by countercurrent contact with the hot product gas. The residue shale was discharged from the bottom of the reactor into a pressurized residue receiver by a second screw feeder. The residue shale was cooled by countercurrent contact with cold feed hydrogen. In a few later runs at high hydrogen rates, the feed hydrogen was preheated.

The feed hydrogen entered the bottom of the reactor at a point above the discharge screw through a dip tube (Figure 8). The exit gas left through a dip tube extending down into the top of the reactor. In later runs, a bayonet filter constructed of sintered metal was installed on the end of the dip tube to remove dust and eliminate plugging of the outlet lines which had occasionally occurred. The feed shale dropped down through a third dip tube which served to keep any heavy liquids in the exit gas from condensing on the feed shale and plugging the tube at the feed screw outlet.

Hydrogen feed gas and hydrogen purge gas were both metered by orifice meters. The shale was fed constantly at the desired rate, and the rate of shale discharge was manually adjusted to give a constant shale-bed level. The shale-bed level was indicated by a nuclear-type level indicator and was recorded continuously. A more accurate measure of the rate of shale feed and discharge was obtained by weighing the shale initially charged to the feed hopper and that present in the feed hopper and residue receiver at the end of the run. Feed and residue shales were analyzed by methods described in Appendix B of IGT Research Bulletin No. 36 (3). The exit-gas volume was measured by a conventional iron-case-type meter. Aliquot samples of the exit gas were collected during the steady-state part of each run. Gas samples were analyzed by mass spectrometer and gas chromatograph. The exit-gas specific gravity was monitored continuously by a recording gravimeter. The product liquids were collected in two different knockout pots and analyzed by conventional ASTM procedures. The first knockout pot (operated at high temperature) contained a short cyclone section, which removed dust and heavy tar. The exit gas was then cooled in a three-stage condenser to condense out low-temperature liquids. These liquids were collected in a low-temperature knockout pot. Both pots were drained, and the collected liquids were weighed every 1/2 hour during the steady-state portion of each run.

All of the tests conducted in the pilot plant were with a single batch of Colorado oil shale from the U.S. Bureau of Mines mine at Rifle, Colorado. Mine run material was crushed to -1/4-inch size at the mine and sieved elsewhere into various fractions. We selected a -6+10 U.S. Standard sieve size material for most of these tests because it was the largest size which we could successfully feed with our existing equipment. This material had a Fischer Assay oil yield in the 20-25 gal/ton range.

Analysis of Oil Shale

A typical analysis of the oil shale used in the tests reported here is given in Table 2.

Table 2. TYPICAL ANALYSIS OF COLORADO OIL SHALE
USED IN BENCH-SCALE TEST PROGRAM

Moisture, wt %	0.30
Composition, wt % (dry basis)	
Organic Carbon	11.30
Mineral Carbon Dioxide	17.55
Hydrogen	1.72
Nitrogen	0.35
Oxygen (By Difference)	1.73
Sulfur	0.54
Ash	<u>66.81</u>
Total	100.00

Screen Analysis, U.S. Standard Sieve Size

	<u>wt %</u>
+6	0.1
+8	12.5
+16	79.9
+30	6.9
+60	0.3
+100	0.1
+200	0.1
-200	<u>0.1</u>
Total	100.0

Effects of Operating Temperature

The first series of tests was conducted to study the effects of reaction zone temperature on the yields and properties of gaseous, liquid, and solid products. These tests were conducted with relatively short (9 to 12 feet) beds and flat temperature profiles. The results of these tests are summarized graphically in Figures 9 and 10.

As expected, gaseous hydrocarbon yields and mineral carbonate decomposition increase with increases in temperature (Figure 9). The results are very encouraging. In all tests, over 90% of the organic carbon was recovered as gaseous and liquid products. At 1200°F, over 80% of the organic carbon was converted to liquids; at 1400°F, over 60% was converted to gas.

The effect of temperature on kerogen conversion is not pronounced although some increase can be noted in the neighborhood of 1300°F. The test at 1200°F was conducted with a shale space velocity considerably higher than that used in the tests at 1300° and 1400°F. More organic carbon removal could probably have been obtained at 1200°F if more residence time had been provided. This higher space velocity probably also caused a relatively lower mineral carbonate decomposition.

The effects of temperature on the lighter (<400°F) liquid product properties are shown in Figure 10. Although less hydrocarbon liquids are formed at the higher temperatures, those formed would be more difficult to gasify. First, the saturates plus olefins content of the IBP <400°F fraction decreases from about 92 volume percent to about 40 volume percent as the temperature increases from 1200° to 1400°F. Also the C/H weight ratio of the entire liquid product increases from an average of about 7.5 to about 11 as the temperature increases from 1200° to 1400°F. Thus, at the higher temperatures, an increasing portion of the liquid product is aromatic. The lighter aromatics, such as benzene, toluene, and xylene, are, of course, very difficult to gasify. The heavier aromatics, however, will produce additional hydrocarbon gases with further reaction. It should be pointed out that the hydrocarbon-type analysis could only be performed on the <400°F fraction of the oils. It should also be pointed out that in no run did the <400°F fraction constitute more than 35% of the total oil.

The liquid products produced in these tests were of substantially better quality than those produced by conventional retorting. In all these tests, at least 89% boiled below 730°F, whereas in conventional retorting processes reported in the literature less than 50% boiled below 800°F.

Because bed heights of about 9 to 12 feet (3-1/2 to 5 heating zones) were used, the feed shale fell through a long heated zone (of 1000°F or more) before reaching the shale bed. This gave an initial rapid heat-up of the shale feed rather than the slow heat-up which would be preferred based on laboratory thermobalance tests. However, based on heat transfer calculations, we estimate that the shale particles reached an average temperature of no greater than about 900°-1000°F by the time they reached the shale bed. Further heating to final bed temperature ranged from about 20° to 30°F/minute, which is more favorable to higher yields.

Effects of Operating Pressure

A second series of tests was conducted to study the effects of reaction zone pressure on the yields and properties of each product. These tests were conducted with a relatively steep temperature gradient in the bed (to prehydrogenate the shale) and bed depths ranging from 12.9 to 15.5 feet (5 to 6 zones). In Figure 11, the product yields are shown as functions of pressure. The product gas yield is only slightly affected by pressure. The liquid products, however, increase with increases in pressure. Thus, the organic carbon remaining in the residue shale decreases with pressure: More than twice as much remains at 125 psig than at 500 psig. The reason for the lower gas yields and higher amounts of residual organic carbon in these runs (compared with previous runs at a 1400° F maximum temperature) is a shorter residence time at high temperature. In these tests, we used a steeper temperature gradient in the upper part of the bed to prehydrogenate the feed shale.

The effects of pressure on hydrocarbon types in the liquid products (<400° F fraction) and the C/H ratio in the total oil are shown in Figure 12. There are only slight effects in the range studied. The olefins fraction decreases and the saturates fraction increases with increases in pressure, but the effect is slight. There is no discernible effect of pressure on the fraction of aromatics. The C/H ratio of the total liquid products also is not significantly affected by pressure. This agrees with the fact that the olefins fraction also remains nearly constant. One would expect a lower C/H ratio at higher pressures because of hydrogenation of the oils. The absence of any oil hydrogenation is probably caused by the low temperatures in the empty space above the bed and within the upper part of the bed, so that the primary liquid products are not hydrogenated.

Mineral Carbonate Decomposition

In tests conducted to show the effects of temperature on the hydrogasification behavior of oil shale, mineral carbonate decomposition ranged from about 26% (at 1200° F maximum reactor temperature) to about 85% (at 1400° F maximum reactor temperature). High mineral carbonate decompositions are undesirable for several reasons. First, the product gas is diluted with carbon oxides, requiring extensive shifting and scrubbing and/or methanation of the product gas. Second, valuable feed hydrogen is consumed by reverse shifting of the carbon dioxide evolved in the carbonate decomposition. Third, the decomposition reaction is endothermic, thus removing sensible heat from the system. Oil shale typically contains large amounts of dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) as well as calcite (CaCO_3). Approximately 36% of the mineral carbon dioxide is present as MgCO_3 in Colorado oil shales, according to the literature (4). We analyzed our oil shale and found the feed material to be about 47% MgCO_3 . From previous studies (3) and from our laboratory thermobalance studies, we found that calcite decomposition can be suppressed by adding CO_2 to the feed gases. However, magnesium carbonate decomposes very rapidly at temperatures above about 1000° F — even in the presence of high partial pressures of CO_2 .

Therefore, later in the test program, we added CO_2 to the feed gas (at about the 5-mole-percent level) in an attempt to reduce total mineral carbonate decomposition (suppress calcite decomposition) since we had been successful in doing so in laboratory thermobalance tests. Mineral carbonate decomposition was reduced about 25% by the addition of CO_2 to the feed gas.

In-Situ Methanation of Carbon Oxides

We noticed, during the bench-scale test program, that carbon oxides were apparently being methanated in the reactor since more hydrocarbons and less carbon oxides were present in the products than would be indicated by carbon and carbon oxides balances. We then carried out two tests with no oil shale present in the reactor and with feed gases containing from about 4 to 6 mole percent carbon dioxide at temperatures and pressures in the region employed in the oil-shale hydrogasification tests. In the first test, we simply passed the feed gas through the reactor tube packed with sand. We found that about 59% of the carbon dioxide was converted to gaseous hydrocarbons (methane and ethane). Since it was possible that the metal reactor tube was catalyzing the reaction rather than the solids, we conducted a second test with an empty reactor tube (to ensure that the methanation observed in our bench-scale tests were indicative of what would happen in a large-scale plant, where the reactor would be refractory-lined and reactor gases would not contact a metallic wall). In this test, only about 18% of the CO_2 was converted to gaseous hydrocarbons, indicating that the metal tube wall was only partially contributing to the observed methanation. Since the gas residence time and gas contact with the metal wall were greater in the latter test than in the first test, it appears that even less of the observed methanation in the bench-scale tests is due to catalysis by the wall.

We also made thermodynamic equilibrium calculations to see how much methane could be formed by methanation of carbon oxides. These calculations show that for all conditions within the reactor tube it is possible (thermodynamically) to form methane in quantities greater than those observed.

SUMMARY AND CONCLUSIONS

Results of the small-scale laboratory thermobalance studies have shown that —

1. The presence of hydrogen, even at low pressure, significantly increases organic carbon recovery as compared with hydrogen-free retorting.
2. Further increases in organic carbon recovery can be achieved at an elevated hydrogen partial pressure. At 500 psia, slow heating can achieve over 95% recovery.
3. The heating rate significantly affects the organic carbon recovery. Very rapid heating to 1300°F limits recovery to about 87%.
4. The carbon dioxide generation by decomposition of CaCO_3 and MgCO_3 begins at about 1000°F, increasing rapidly above this temperature. Decomposition of the CaCO_3 can be almost completely suppressed by the addition of small amounts of CO_2 in the feed gas stream; MgCO_3 decomposition cannot be suppressed at hydrogasification temperatures.

Results obtained in the 4-inch-diameter reactor have generally verified the trends observed in the laboratory study. Kerogen recoveries using hydrogen have exceeded 90% — significantly better than recoveries obtained in conventional retorting.

Constant-temperature runs (rapid shale heat-up in free fall above the bed) indicate that high temperature favors the production of gas and promotes aromatization of the liquid products.

The use of controlled shale heat-up (shale preheated in the upper portion of the bed) favors liquid production; however, the liquid products are of much higher quality.

Additional data obtained in the countercurrent tests verified the ability to suppress carbonate decomposition by adding CO₂ to the feed hydrogen. We also discovered that substantial methanation of carbon oxides occurs in the shale bed.

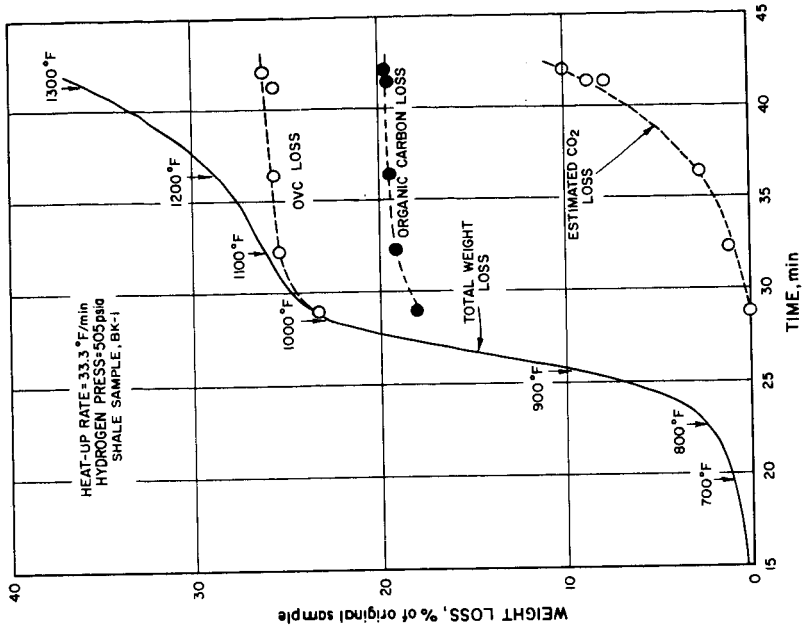
In summary, the experimental program has shown that the basic concept of countercurrent operation is technically feasible. The overall chemistry of the system is now better defined and looks very favorable.

ACKNOWLEDGMENT

The work described here was sponsored by the American Gas Association. The authors wish to express their appreciation to the Association for permission to publish this paper. We also wish to express our appreciation to Mr. H. W. Sohns and Mr. M. D. Smith of the U.S. Bureau of Mines who provided us with the oil shale used in this program.

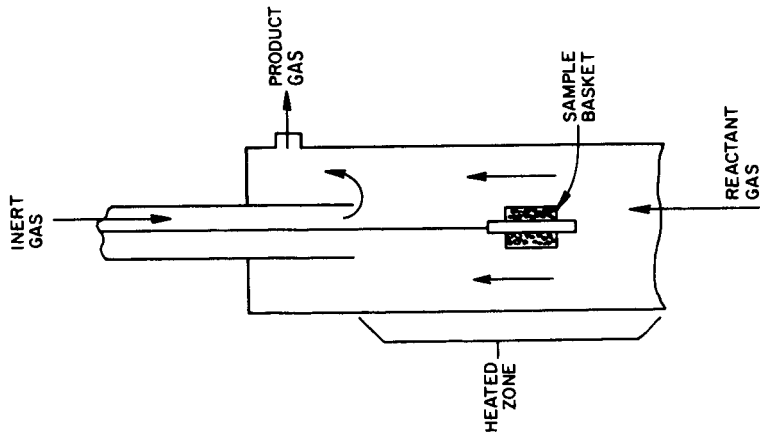
LITERATURE CITED

1. Dirksen, H. A. and Lee, B.S., "Balanced-Pressure Pilot Reactor," Chem. Eng. Progr. **62**, 98-102 (1966) June.
2. Feldkirchner, H. L. and Johnson, J. L., "High Pressure Thermobalance," Rev. Sci. Instrum. **39**, 1227-29 (1968) August.
3. Feldman, H. F., Bair, W. G., Feldkirchner, H. L., Tsaros, C. L., Shultz, E. G., Jr., Huebler, J. and Linden, H. R., "Production of Pipeline Gas by Hydrogasification of Oil Shale," IGT Res. Bull. No. **36**. Chicago, 1966.
4. Stanfield, K. E. et al., "Properties of Colorado Oil Shale," U.S. Bureau of Mines Rep. Invest. **4825**. Washington, D.C., November 1971.



A-13-107

Figure 2. TYPICAL WEIGHT -
LOSS CURVE FOR RICH SHALE



A-71731

Figure 1. THERMOBALANCE REACTOR

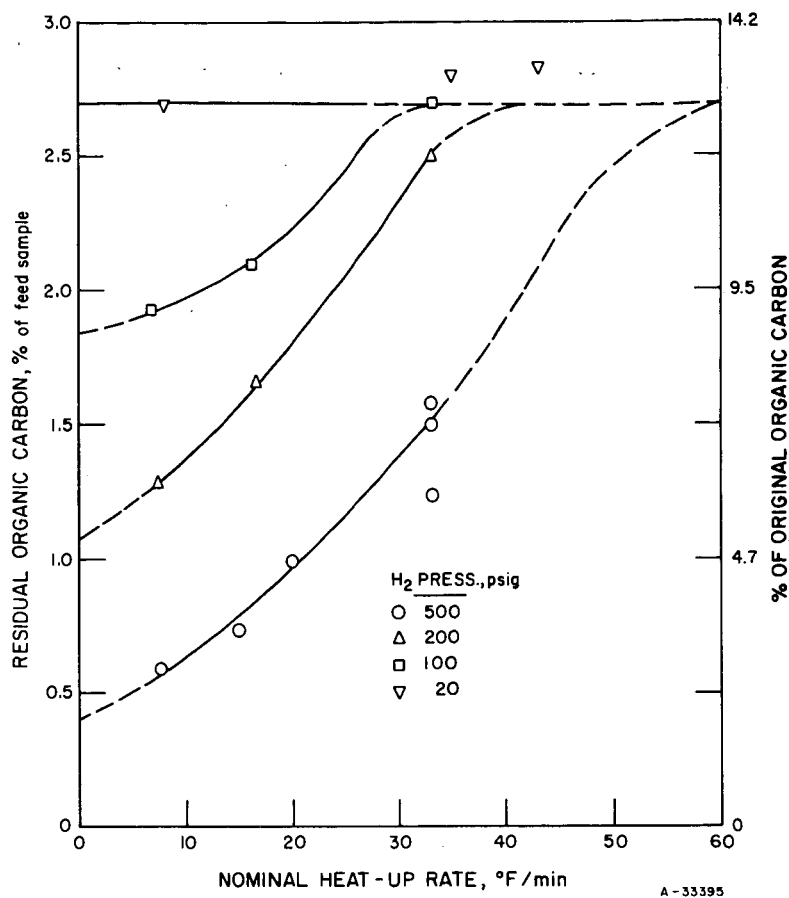
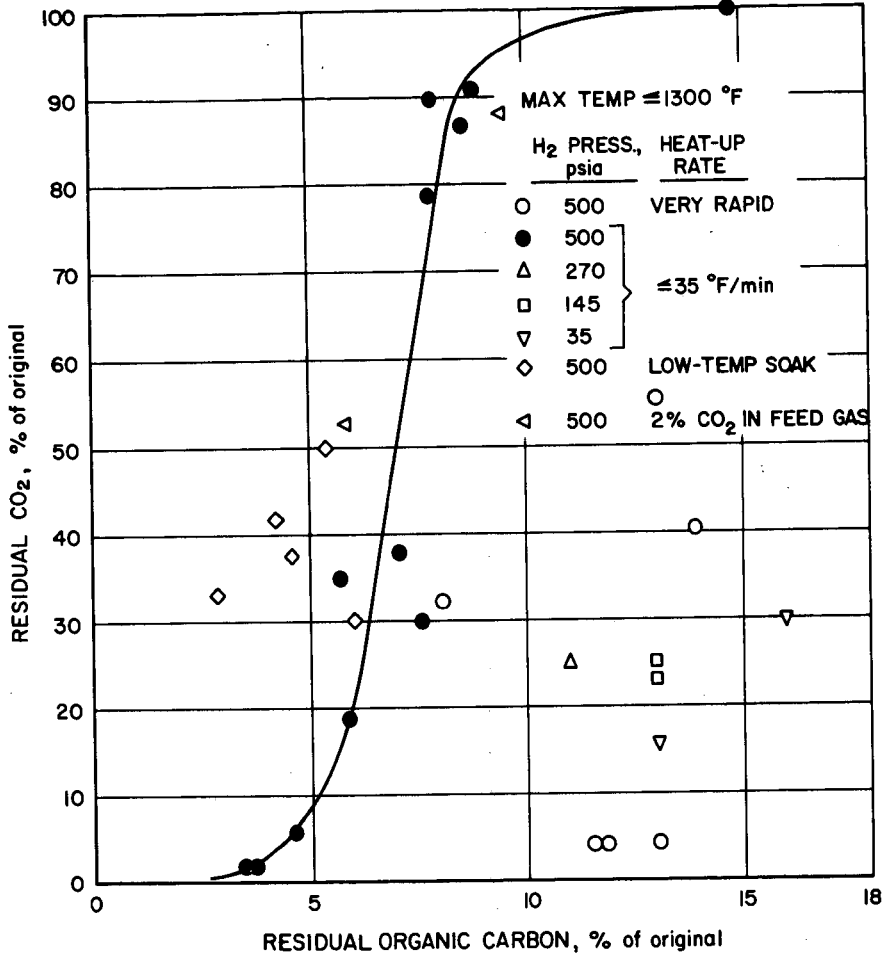
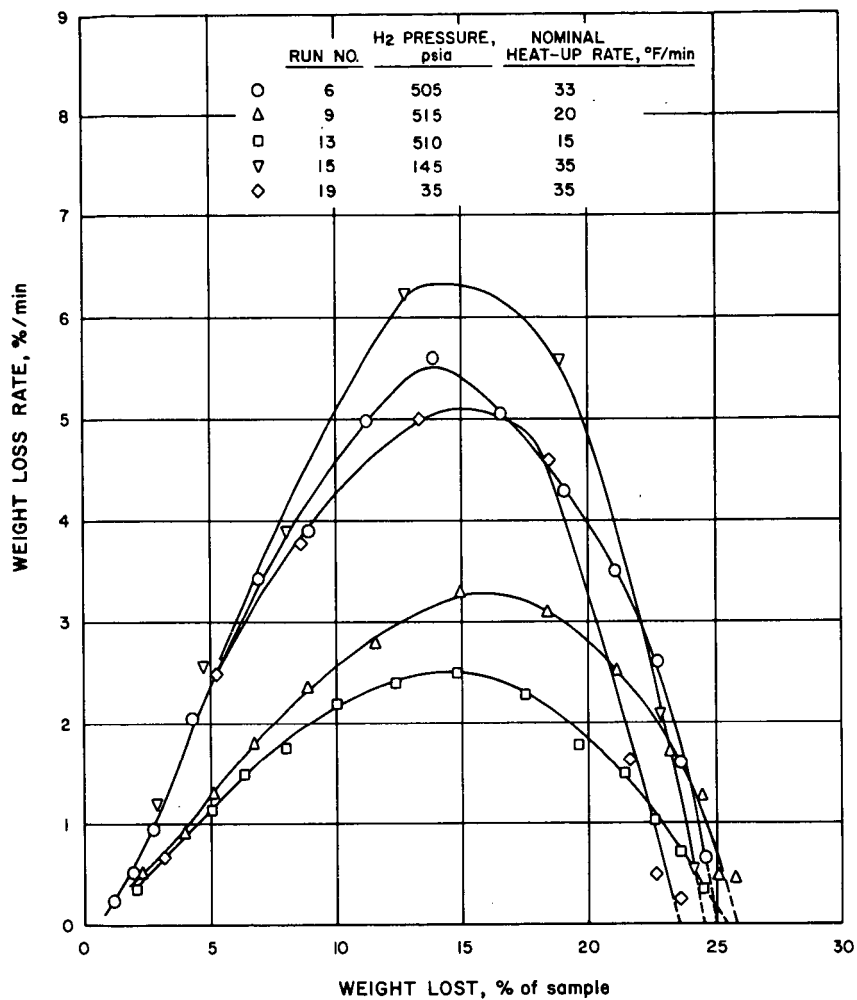


Figure 3. PRESSURE EFFECT ON KEROGEN RECOVERY FROM RICH SHALE IN PURE HYDROGEN ATMOSPHERES



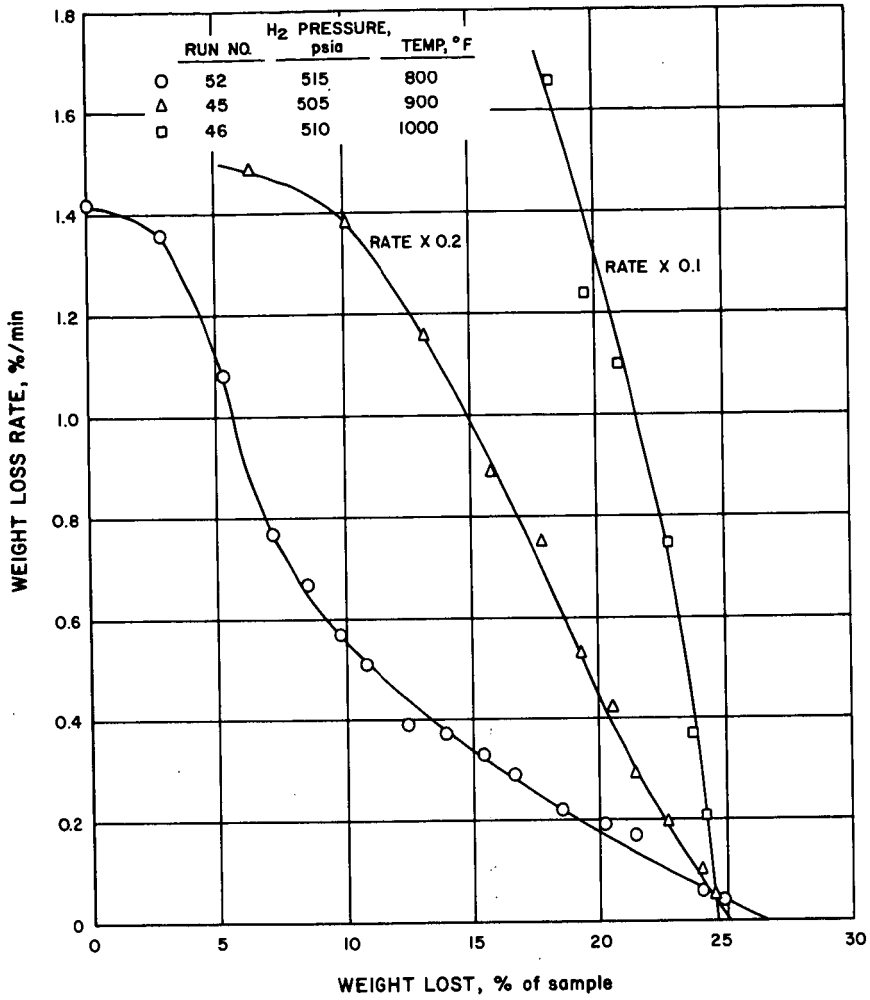
D-103-1544

Figure 4. CORRELATION OF RICH SHALE KEROGEN RECOVERY AND CARBONATE DECOMPOSITION IN PURE HYDROGEN



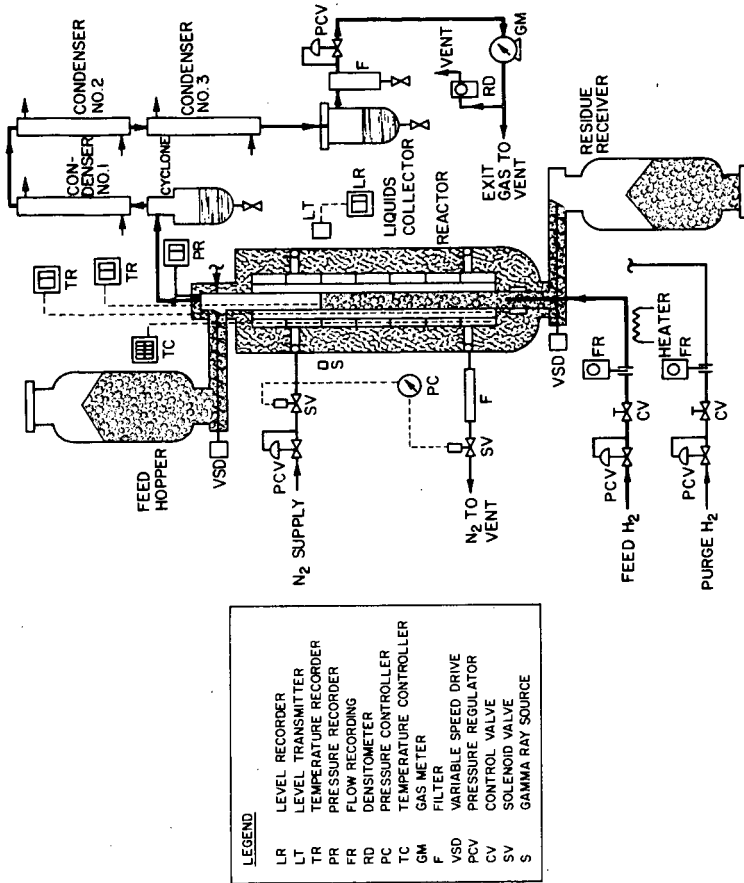
A-13-98

Figure 5. LOW-TEMPERATURE WEIGHT LOSS OF RICH SHALE (Heat-Up Runs)



A-13-97

Figure 6. LOW-TEMPERATURE WEIGHT LOSS OF RICH SHALE (Constant-Temperature Runs)



E-93-1409

Figure 7. FLOW AND INSTRUMENTATION DIAGRAM FOR HIGH-TEMPERATURE BALANCED-PRESSURE BENCH-SCALE UNIT

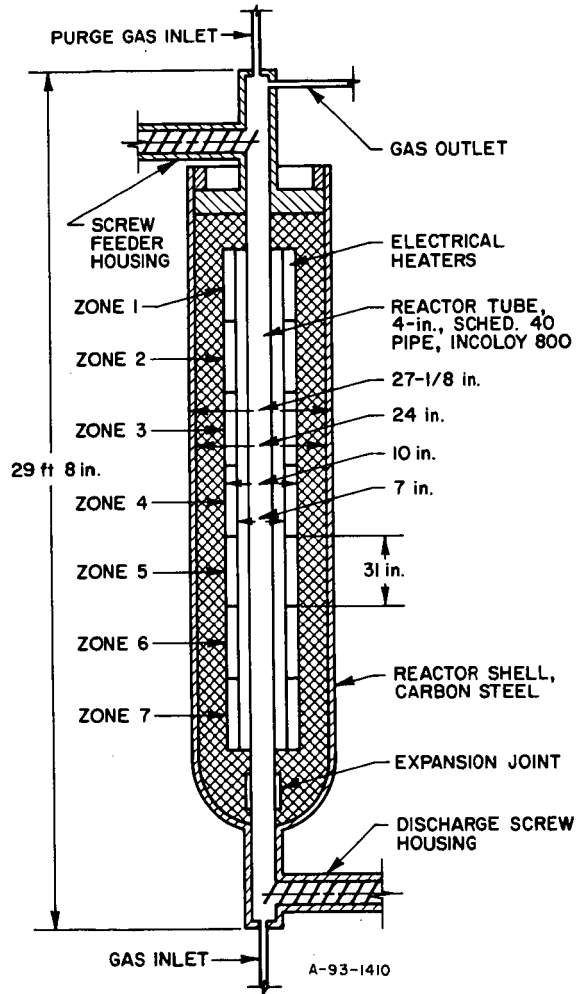


Figure 8. HIGH-TEMPERATURE BALANCED-PRESSURE REACTOR

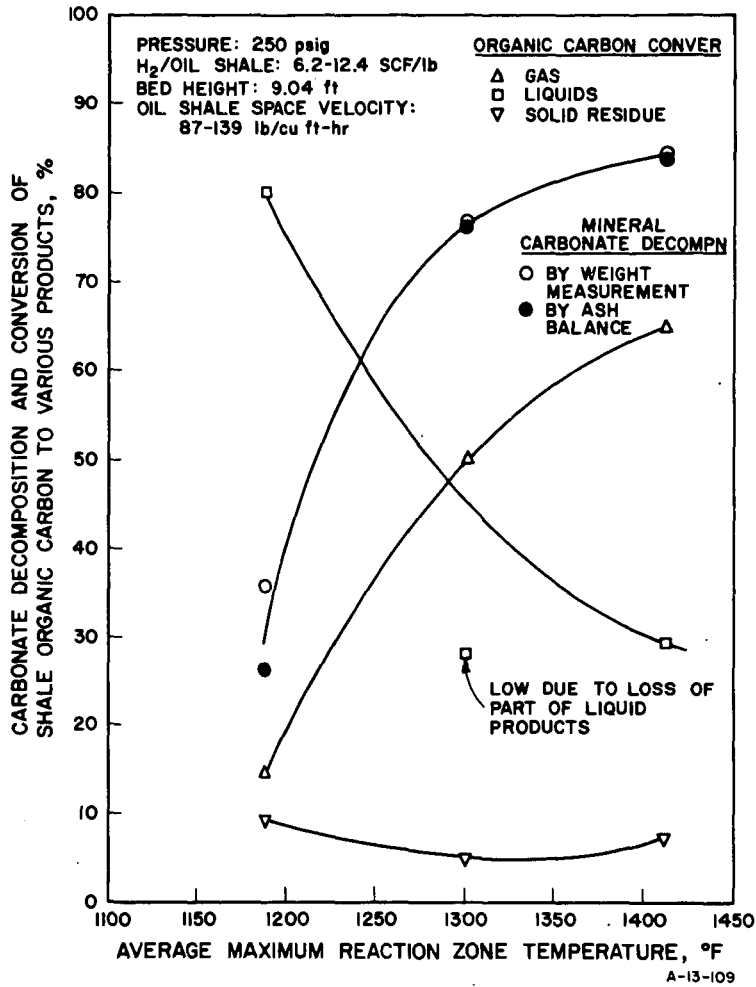


Figure 9. PRODUCT DISTRIBUTION IN BENCH SCALE TESTS

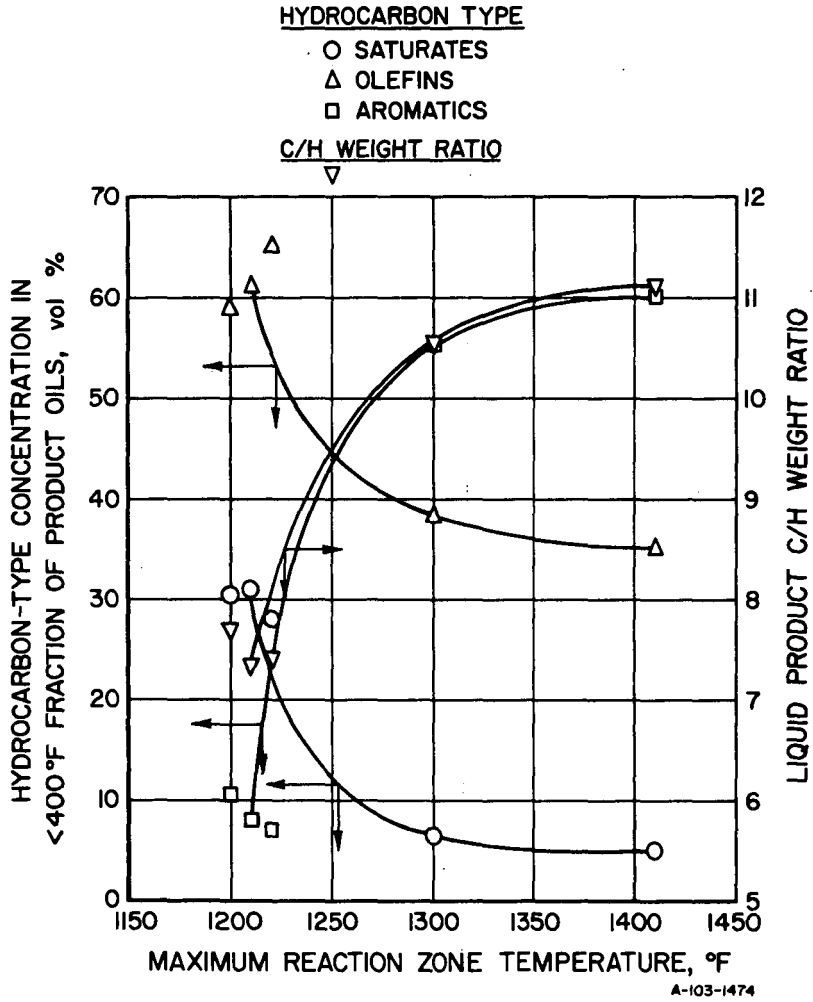


Figure 10. EFFECTS OF REACTION ZONE TEMPERATURE ON LIQUID PRODUCT PROPERTIES

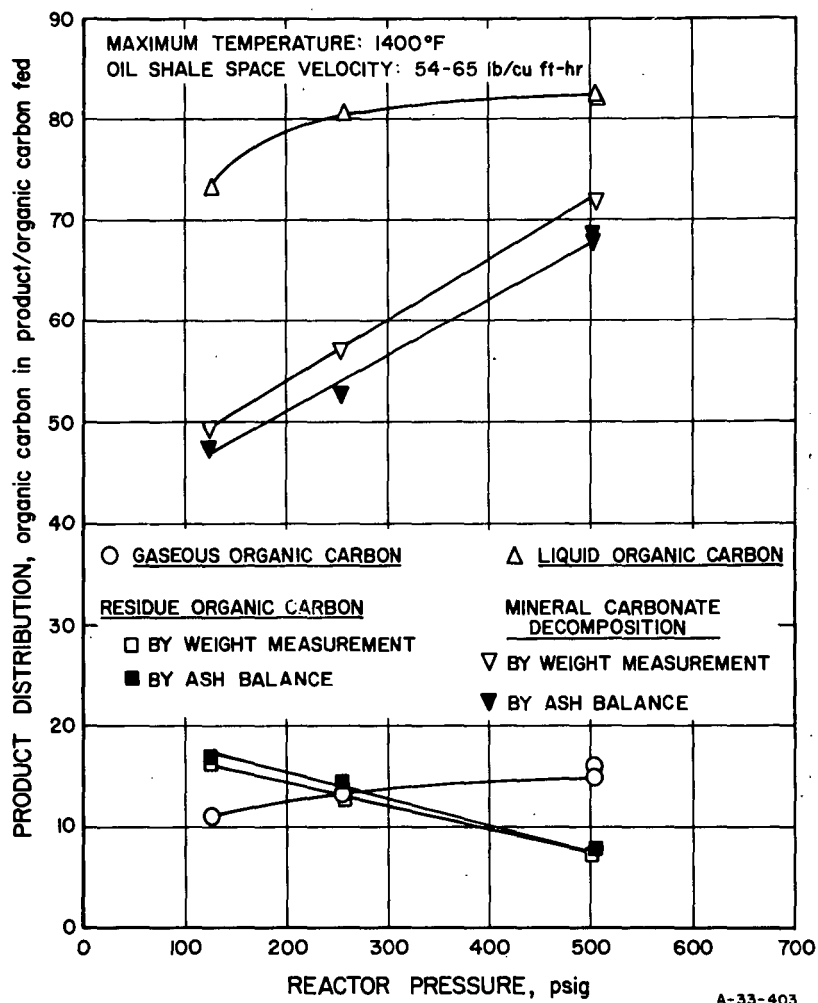


Figure 11. EFFECT OF PRESSURE ON ORGANIC CARBON DISTRIBUTION IN PRODUCTS AND MINERAL CARBONATE DECOMPOSITION

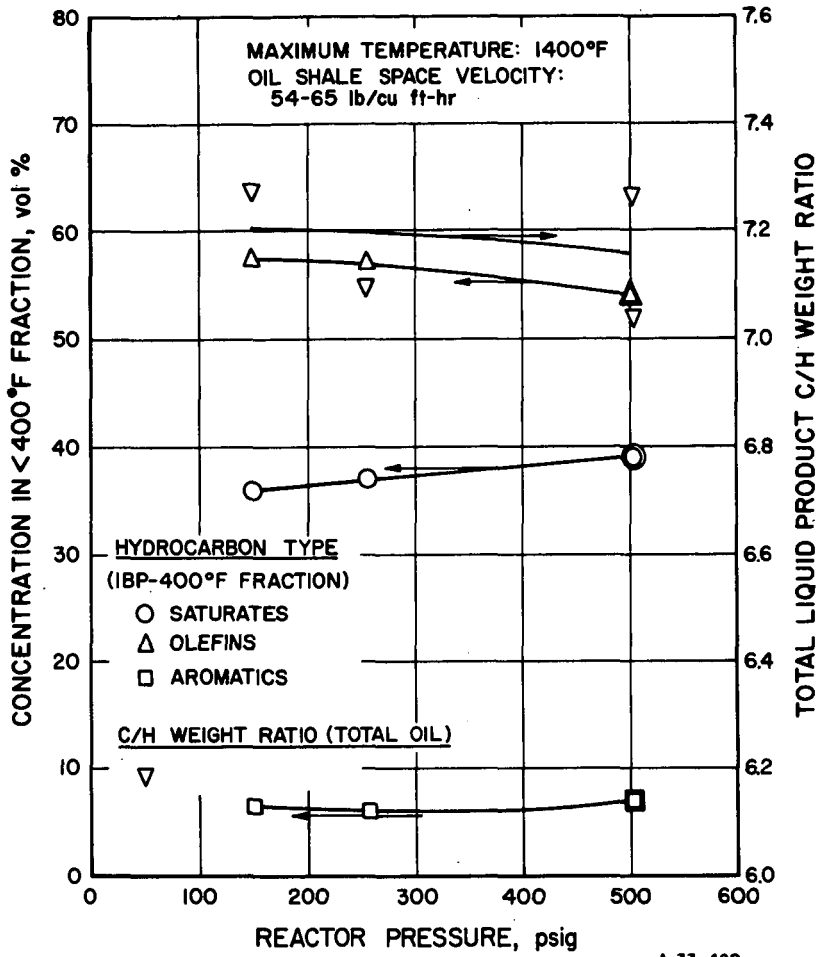


Figure 12. EFFECT OF PRESSURE ON LIQUID PRODUCT PROPERTIES